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(54) LIQUID DETERGENT COMPOSITION

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to an aqueous detergent composition containing a non-ionic surface-active detergent and a gelatin having a molecular weight of at least 12 500, and a gel strength of at least 25 Bloom grams. Specifically, it pertains to an aqueous detergent composition designed in particular for cleaning glassware, china, and glazed or vitreous articles, providing outstanding drainage characteristics, avoiding towel-drying and substantially minimizing the filming, streaking, spotting of the washed, rinsed and air-dried articles, containing a nonionic surface-active detergent and hydrosoluble gelatin, having a molecular weight of from 2 500 to 200 000, preferably of from about 25 000 to 80 000, a gel strength of from 25 to 300, preferably of from 80 to 200 Bloom grams, and an isoelectric point between pH 4.5 and 9.2.

The performance of a detergent composition in cleaning glasses, dishes, windows and other articles with glazed surface is usually evaluated by the consumer in terms of shine, non-filming, non-spotting, non-streaking. The liquid, dishwashing detergent compositions presently on the market are mainly designed to remove the soils from said glasses, dishes, windows, but the detergent solution- and redeposited soil residues then have to be removed from the washed articles by rinsing and/or towelling when still wet. If not rinsed and towel-dried immediately, these residues dry upon the surfaces of the washed articles, leaving hard-to-remove spots, films or streaks.

In case the articles are washed and/or rinsed in plain water, and not towel-dried immediately, additional water hardness spots and streaks appear on the washed and rinsed surfaces upon evaporation of the water.

Towel-drying of washed articles, e.g. glasses, dishes, immediately after being taken out of the washing and rinsing liquors, is uneconomic (more towels are required) and is not always possible (too frequent interruption of the washing). Therefore, many housewives simply put the washed or washed and rinsed articles aside for dripping and air-drying. Consequently, the cleaning efficiency of the product used, which the housewife may have visually appreciated at the end of the washing or rinsing cycle, is lost due to dried, hard-to-remove, unpleasant, adhering or redeposited detergent-, soil-, and/or water hardness residues of the washing liquor or rinsing water.

The cleaning of larger glazed surfaces as tiled walls, e.g. in a shower-room, or ceramic bath tubs, wash-basins or other similar items having a vitreous surface, also requires wiping or rinsing and wiping when still wet, to avoid spotting, filming and streaking. Wiping immediately after cleaning to avoid evaporation and consequently spotting, streaking and filming, is not always feasible and requires a frequent interruption of the cleaning process. Therefore, the cleaners may be considered as not cleaning well, although the soil may have been removed in the first instance, because of the streaks, film, and spots left on the treated surfaces.

Attempts have been made to minimize the effect of detergent-, soil-, and/or water hardness residue deposition during air-drying by employing various additives at either the washing or rinsing stage of the cleaning cycle, by either complexing the water hardness salts, adding improved soil-suspending agents, or formulating special rinsing agents. The incorporated complexing and/or soil suspending

agents in liquid detergent compositions create formulation difficulties, while the special rinsing agents have to be packed and applied separately.

5 It has now been surprisingly found that the combination of a small amount of gelatin having a gel strength of at least 25 Bloom grams, a molecular weight of at least 12 500, and an iso-electric point between pH 4.5 and pH 9.2, and a nonionic surface-active detergent, optionally containing other specific surface-active agents and/or builder salts in well-defined amounts, yields outstanding washing and cleaning agents especially suitable for cleaning glassware, china, and glazed or vitreous articles, providing outstanding drainage characteristics, avoiding towel-drying, substantially minimizing filming, streaking or spotting the washed, cleaned, rinsed and air-dried glassware, china and glazed or vitreous articles.

Detergent compositions containing gelatin or hydrolyzed proteins and surface-active detergents are, for example, described in the British patent specification 1 160 485, the Italian patent specification 862 247, or the German patent application 1 929 040. In said British patent specification the described lotions or detergent compositions contain partially degraded protein having a gel strength of zero Bloom grams. A gelatin with a gel strength of zero Bloom grams is completely unsuitable for the detergent composition of the present invention. The gelatin present in the detergent compositions mentioned in the Italian or German patent specification cannot be incorporated into the liquid detergent composition of the present invention, while the surface-active detergent system and other mandatory components will inhibit the drainage.

If there is a continuing need for washing and cleaning compositions, in particular dishwashing compositions, to remove the soil residues and to improve the final dry appearance, there is certainly a continuing need for a compatible combination of materials which will simultaneously provide cleaning, improved final dry appearance making towel-drying or wiping superfluous. Therefore, it is an object of the present invention to provide a liquid, aqueous detergent composition for glazed or vitreous items, with excellent cleaning performance and improved drainage after rinsing, thereby avoiding staining of the washed, rinsed and air-dried glazed or vitreous surfaces, making towel-drying or wiping superfluous.

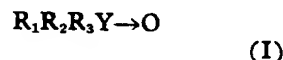
The attractivity, efficacy and economy of the composition of the present invention can—and this is another valuable aspect of this invention—be improved, adapted, tailored to suit specific needs by admixing additional, water-soluble, organic, anionic surface-active detergents, water-soluble, organic acids or salts thereof; emulsifying agents; bactericides;

dyes; perfumes; corrosion inhibitors; soil suspending agents, as more specifically indicated hereinafter.

The liquid detergent composition of this invention contains

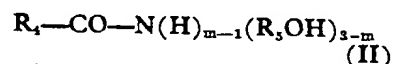
(A) from 2% to 40% by weight of a water-soluble, organic, nonionic surface-active detergent chosen from the group consisting of:

(1) tertiary oxides corresponding to the general formula



wherein R_1 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon-, hydroxy-hydrocarbon- or alkyl-oxyhydrocarbon radical having in total from 8 to 24 carbon atoms; and R_2 and R_3 are each a methyl-, ethyl-, hydroxymethyl-, or hydroxyethyl radical; and Y is a N or P;

(2) amides corresponding to the general formula



wherein R_4 is a saturated or unsaturated, aliphatic hydrocarbon radical having from 7 to 21 carbon atoms; R_5 represents a methylene or ethylene group; and m is 1, 2, or 3;

(3) a condensation product of from 3 to 25 moles of ethylene oxide and one mole of an organic, hydrophobic compound, aliphatic or alkyl aromatic in nature, having from 8 to 24 carbon atoms; or a mixture thereof; and

(B) from 0.1 to 5% by weight of a water-soluble gelatin, having a molecular weight of at least 12 500, a gel strength between 25 and 300 Bloom grams, and an iso-electric point between pH 4.5 and pH 9.2.

The nonionic surface-active detergents to be used in the formulation of a liquid detergent composition of this invention, the gelatin, and the other ingredients which can be added thereto are described hereinafter. If, in said description of additional surface-active detergents and ingredients, reference is made to a salt, then reference is made to either the sodium, potassium, ammonium, trimethyl-, triethyl-, dimethyl-, diethyl-, trimethanol-, triethanol-, dimethanol- and diethanol ammonium salts, if not specified otherwise.

Gelatin being a typical protein (obtained from collagen by boiling skin, ligaments, bones, etc. with water), the gelatin molecules, like the molecules of other proteins, are large and complex, having an average molecular weight ranging from about 5 000 up to 200 000 and above. Gelatin molecules, charged when in alkaline or acidic solution, and thus amphoteric in character, have a specific iso-electric point, which depends mainly upon the processing conditions in manufacturing. Gelatin obtained by

acid treatment has an iso-electric point generally between pH 7 and pH 9. Gelatin obtained by alkaline treatment has an iso-electric point normally between pH 4.6 and 5. By using special treatments, gelatins having an iso-electric point as low as pH 4.5 and as high as pH 9.2 can even be obtained, and by mixing gelatins having different iso-electric points, any gelatin mixture having an iso-electric point between pH 4.5 and pH 9.2 can be formulated.

The amount of water-soluble gelatin to be included in the liquid detergent composition of the present invention may vary between 0.1% and 5% by wt, preferably between 0.2% and 2% by wt, calculated on the total weight of the composition. If the very low level of 0.1% by wt is necessary to obtain still a noticeable drainage effect, the highest level is restricted to 5% by weight, due to formulation requirements, i.e. to have a liquid composition which is still pourable and, consequently, easy to handle, to dissolve and to apply.

To obtain said overall cleaning effect, i.e. removal of soil by simple washing and removal of soil-, surface-active detergent- and water hardness residues due to drainage after additional rinsing, but without wiping or towel-drying, the molecular weight of the water soluble gelatin to be used in the liquid detergent composition of this invention must be above 12 500, preferably above 15 000, preferably between 25 000 and 80 000, and most preferably between 35 000 and 50 000, while the iso-electric point of the gelatin must be between pH 4.5 and pH 9.2, preferably pH 6 or higher, and most preferably between pH 7 and pH 9, while the gel strength of the gelatin used must be above 25 Bloom grams, preferably above 50, most preferably between 80 and 200 Bloom grams (gel strength in Bloom grams or Bloom strength is the force in grams to be applied on a cylinder, diameter 12.7 mm, on the free surface of a gel of 6.67% gelatin having a 15% humidity, to force it 4 mm into the gel; reference: British Standard Method for Sampling and Testing Gelatins).

Since the detergent compositions of the present invention exist in liquid form, such compositions can appropriately contain stabilizing agents such as certain hydrotropes and/or electrolytes to promote phase stability. Commonly employed hydrotropes include conventional lower alkylaryl sulfonates such as sodium and potassium toluene sulfonate, xylene sulfonate, benzene sulfonate and cumene sulfonate. Lower alkanol hydrotropes such as methanol, ethanol, propanol and butanol can also be employed as hydrotropes in the present invention but are not preferred. Electrolyte salts such as potassium chloride can also optionally be added to improve phase stability of the liquid detergent compositions. When employed, the above described hydrotropes

and/or electrolytes generally comprise from 1% to 40%, preferably from 2% to 12% by weight of the total composition.

The addition of some synthetic, anionic, surface-active detergents, when added in given amounts to the liquid detergent composition of the present invention, decreases the rinsing time needed to obtain effective drainage performance. Said phenomenon permits the formulation of liquid detergent compositions containing additionally anionic surface-active detergents (in amounts up to 40% by weight) specially for use in water of medium to high ionic strength (ionic strength=concentration in the washing liquor of metallic cations as Ca^{2+} , Mg^{2+} , mainly due to water hardness; Na^+ , K^+ , etc. for some builders).

Suitable, hydrosoluble, nonionic surface-active detergents to be used in the formulation of the liquid detergent composition of the present invention are:

- (1) water-soluble, nonionic, tertiary amine oxides as represented hereinafter by the general formula



(I)

whereby Y represents a N-atom, the arrow is a conventional representation of a semi-polar bond; R_1 represents a high molecular, straight or branched, saturated or unsaturated, aliphatic hydrocarbon-, hydroxyhydrocarbon- or alkoxyhydrocarbon radical, preferably an alkyl radical, having in total 8 to 24, preferably 12 to 18, most preferably 12 carbon atoms, or a mixture of dodecyl with decyl- and tetradecyl radicals, whereby at least 50% of the radicals are dodecyl; R_2 and R_3 , which may be the same or different, represent each a methyl-, ethyl-, hydroxymethyl- and hydroxyethyl radical. They are generally prepared by direct oxidation of appropriate tertiary amines, according to known methods. Specific examples of tertiary amine oxides are: dimethyl dodecyl amine oxide, diethyl tetradecyl amine oxide, bis - (2 - hydroxyethyl) - dodecyl amine oxide, bis - (2 - hydroxyethyl) - 3 - dodecoxy - 1 - hydroxypropyl amine oxide, dimethyl 2-hydroxy-dodecyl amine oxide, and diethyl cicosyl amine oxide;

- (2) water-soluble, nonionic, tertiary phosphine oxides as represented hereinafter by the general formula

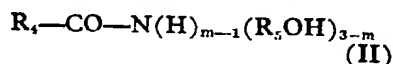


(I)

but whereby Y stands for a phosphorous atom, R_1 , R_2 and R_3 have the same meaning as hereinbefore, and the arrow is a conventional representation of a

semi-polar bond, and which can be prepared by alkylating an alkyl phosphine derivative and oxidizing said reaction product as described for example in the French patent specification 1317586. Specific examples of tertiary phosphine oxides are: dimethyl dodecyl phosphine oxide, diethyl tetradecyl phosphine oxide, bis - (2 - hydroxyethyl) - dodecyl phosphine oxide, tetradecyl methyl 2-hydroxyethyl phosphine oxide, oleyl dimethyl phosphine oxide, and 2-hydroxy-dodecyl dimethyl phosphine oxide;

(3) water-soluble amides as represented hereinafter by the general formula



wherein R_1 is a saturated or unsaturated, aliphatic hydrocarbon radical having from 7 to 21, preferably from 11 to 17 carbon atoms; R_2 represents a methylene or ethylene group; and m is 1, 2, or 3, preferably 1. Specific examples of said amides are mono-ethanol coconut fatty acid amide, diethanol dodecyl fatty acid amide, and dimethanol oleyl amide;

(4) water-soluble condensation products obtained by condensing, in a manner known per se, from 3 to about 25 moles ethylene oxide with one mole of an organic, hydrophobic compound, aliphatic or alkyl aromatic in nature, having 8 to 24 carbon atoms and at least one reactive hydrogen atom, preferably a reactive hydroxyl, amino, amido, or carboxy group. General examples are:

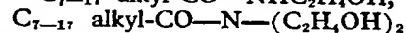
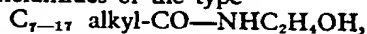
(a) the condensates of ethylene oxide with aliphatic alcohols of more than eight carbon atoms. The alcohols can be derived from the naturally occurring fatty acids, but also from various branched-chain higher alcohols. Among the preferred alcohol-ethylene oxide condensation products are those made from alcohols derived from tallow- and coconut fatty acids. Most preferred are condensation products of about 4 to about 12 moles of ethylene oxide per mole of an aliphatic alcohol having from 10 to about 18 carbon atoms, in particular a middle-cut coconut fatty alcohol condensed with 6 moles of ethylene oxide;

(b) condensates of ethylene oxide with alkylphenols, whereby the phenol may be mono- or polyalkylated and the total number of side-chain carbons atoms is as low as 5 to as high as 18 carbon atoms. The aromatic nucleus bearing the phenolic hydroxyl may be benzene, naphthalene, or diphenyl, preferably benzene. Specific examples are condensation products of one mole nonylphenol with 9 to 15 moles of ethylene oxide;

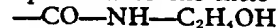
(c) condensates of ethylene oxide with the fatty acid esters, preferably mono-fatty acid esters of the sugar alcohols, sorbitol and manitol, and—but less preferred—of di- and polysaccharides. Specific examples are the polyoxyethylene sorbitan-monolauric acid esters, having 20 and more ethylene oxide units; and the polyoxyethylene derivatives of fatty acid partial esters of hexitol anhydrides generally known under the Registered Trade Mark TWEEN;

(d) polyethynoxy esters or esters by reacting ethylene oxide with carboxylic acids. The acids can be natural fatty acids or fatty acids made from oxidized paraffin wax, or mono- or polyalkylated benzoic and naphthenic acids. Preferred are aliphatic fatty acids having from 10 to 20 carbon atoms, and benzoic acids with 5 to 18 carbon atoms in the alkyl groups. Specific examples and preferred condensation products are tall oil-ethylene oxide and oleic acid-ethylene oxide condensation products having 9 to 15 ethylene oxide units;

(e) condensation products of fatty acyl alkanolamides of the type



with ethylene oxide. Preferred are condensation products of one mole coconut



with 5 to 20 moles of ethylene oxide. Specific examples of polyethenoxo alkanolamides of fatty acids are the commercial products, marketed under the Registered Trade Mark ETHOMID.

(f) condensation products of C_{4-18} alkyl-, C_{8-18} alkenyl- and C_{3-18} alkyl-aryl amines and ethylene oxide. A specific and preferred example is the condensation product of one mole of a dodecylamine with 9—12 moles of ethylene oxide. Another specific example has the formula $C_{11-13} \text{ alkyl-CO-NH-C}_6\text{H}_4\text{-N-[(OC}_2\text{H}_4)_6\text{OH]}_2$.

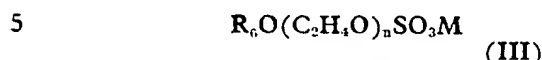
The levels of nonionic surface-active detergent in the liquid detergent composition of the present invention should not be higher than 40% by wt.

As said hereinbefore, the attractiveness, efficacy and economy of the composition of the present invention can be improved, adapted or tailored to suit specific needs, by admixing additional, water-soluble, organic, anionic, surface-active detergents, water-soluble organic acids or salts, etc. As previously explained, one specific advantage of admixing synthetic, organic, anionic surface-active detergent is a decrease in the rinsing time needed to obtain the optimum drainage performance.

Suitable, organic, synthetic, anionic surface-active detergents which can be added or be

present in the liquid detergent composition of the present invention are:

- (5) water-soluble hydrocarbon sulfates having the general formula



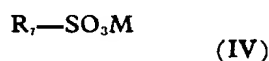
wherein R_n is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 22 carbon atoms; n is from 0 to 15; and M is a cation, preferably sodium or potassium. Important examples which form part of the preferred composition of the present invention are the salts of an organic, sulfuric acid reaction product of a saturated or unsaturated fatty alcohol having 8 to 18 carbon atoms, preferably tallow or coconut alcohol, reacted with 1.5 to 15, preferably 3 to 12 moles of ethylene oxide per mole of fatty alcohol. Specific examples are C_{12-14} alkyl-

$O-(C_2H_4O)_3-SO_3N(C_2H_4OH)_3$;
coconut- $O-(C_2H_4O)_4-SO_3Na$; C_{14}
alkyl- $O-(C_2H_4O)_3SO_3NH_4$; C_{12-16}
alkyl- $O-(C_2H_4O)_6-SO_2K$; and tal-

low- $O-(C_2H_4O)_9-SO_3N(H)(C_2H_4OH)_2$.

Important examples of hydrocarbon sulfates as represented hereinbefore by the general formula (III) whereby $n=0$, are those obtained by sulfating hydroxylated hydrocarbons, preferably fatty alcohols having 8 to 18, most preferably 12 to 16 carbon atoms, with SO_3 , H_2SO_4 , etc., followed by hydrolysis and/or bleaching according to processes well known in the art;

- (6) water-soluble salts of the organic, sulfuric acid reaction products of the general formula



wherein R_7 is chosen from the group consisting of a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24, preferably from 12 to 18 carbon atoms; and an alkylbenzene radical having from 8 to 18, preferably from 12 to 16 carbon atoms in the alkyl group; and M is a cation. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the salts of an organic, sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, meso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 12 to 18 carbon atoms; or of a hydrocarbon of the ethylene series, having 8 to 20, preferably 12 to 18 car-

bon atoms, and 1 up to 4 double bonds, and a sulfonating agent, e.g. SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are sulfonated C_{12-18} n-paraffins, alone or in combination with sulfonated α -olefins containing in average 14 carbon atoms. Important examples of alkylbenzene sulfonates in which the alkyl group contains from 9 to 18 carbon atoms, are dodecyl-, tetradecyl- and hexadecylbenzene sulfonates and those described in the United States Letters Patents Nos. 2 220 099 and 2 477 383.

The maximum level of water-soluble, anionic surface-active detergents that can be included in the liquid detergent composition of the present invention is conditioned by the level of nonionic surface-active detergent present and also to a certain extent by the presence of the gelatin. Therefore, the maximum amount of both nonionic and anionic surface-active detergents which can be present in the composition of the present invention is about 48% by wt, calculated on the total weight of the composition.

The preferred anionic, surface-active detergent which can be included in the composition of the present invention, is the water-soluble hydrocarbon sulfate as represented hereinbefore by the general formula $R_nO(C_2H_4O)_nSO_3M$ (III), wherein R_n is preferably straight, saturated, aliphatic hydrocarbon radical, having from 8 to 20, preferably 12 to 16 carbon atoms; n is preferably from 1.5 to 12, most preferably from 3 to 9; and M is preferably sodium sodium or potassium. Said preferred ethoxylated hydrocarbon sulfates can be present in amounts up to 40%, but preferably between 5 and 20% by wt, calculated on the total weight of the composition.

In case water-soluble salts of the organic, sulfuric acid reaction product of the general formula R_7-SO_3M (IV), wherein R_7 is chosen from the group consisting of a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical, having from 8 to 24, preferably from 12 to 18 carbon atoms; and an alkylbenzene radical having from 8 to 18, preferably from 12 to 16 carbon atoms in the alkyl group; and M is a cation; are incorporated in the liquid detergent composition of the present invention, the maximum amount should be lower than 30% by wt, calculated on the total weight of the composition, and should preferably not exceed 20% by wt. Preferred compounds are the sulfonated C_{12-18} n-paraffins, alone or in combination with sulfonated C_{12-18} α -olefins.

In case of combinations of water-soluble, ethoxylated hydrocarbon sulfates, as represented hereinbefore by the general formula $R_nO(C_2H_4O)_nSO_3M$ (III) and water-soluble salts of the organic, sulfuric acid reaction pro-

duct of the general formula R_nSO_3M (IV), wherein R_n , R , M and n have the meaning indicated above; the weight ratio of said water-soluble salts of the organic, sulfuric acid reaction product to the sum of both the nonionic surface-active detergent and ethoxylated hydrocarbon sulfate should preferably be, dependent upon the concentration and type of the metal cations present in the washing liquor (i.e. the ionic strength) at most 3/1, most preferably be below 1.5/1. Most preferred are those compositions whereby the water-soluble ethoxylated hydrocarbon sulfates are C_{12-18} alkyl- $O-(C_2H_4O)_{3-6}SO_3M$, the water-soluble salts of the organic, sulfuric acid reaction products are C_{12-18} paraffin sulfonate the nonionic surface-active detergent is a mixture of C_{12-14} alkyl-dimethyl amine oxide and coconut fatty acid diethanol amide, whereby the weight ratio of paraffin sulfonates to the sum of C_{12-18} alkyl- $O-(C_2H_4O)_{3-6}SO_3M$ plus amine oxide and fatty acid diethanol amide is at most 2/1, preferably 1/1.

To improve the greasy soil emulsification, other nonionic surface-active agents, such as polyethylene glycol condensation products having a molecular weight of from 160 to 1200, and/or fatty acid esters, preferably mono-fatty acid esters of sugar alcohols, sorbitol and manitol can be incorporated in the composition of the present invention. If the amount of polyethylene glycol condensation products can be as high as 15% by wt, preferred are amounts of 2% to 8% by wt. The highest amount of the fatty acid esters of sugar alcohols is conditioned by their solubility and should preferably not exceed 3% by wt, calculated on the total weight of the composition. Another component that can be included in the cleaner composition of this invention is a water-soluble, low molecular, organic acid, or the water-soluble alkali-metal, ammonium-, and substituted ammonium salts thereof. Suitable water-soluble, low molecular, organic acids and salts thereof, including both the partially neutralized and completely neutralized salts, are for example acetic-, citric-, malic-, gluconic-, maleic-, lactic-, tartaric-, propionic-, butyric-, malonic-, polymaleic-, polyitaconic-, glutaric-, citraconic acid; benzene pentacarboxylic- and hexacarboxylic acid; succinic acid, ethylene diamine tetra-acetic acid, nitrilotri-acetic acid. Said organic acids and/or the salts thereof are added to enhance the cleaning action of the liquid detergent composition of the present invention, and can in addition be used as a source of ions to keep the pH of the composition at a given pH value.

Specific examples of suitable, water-soluble, partially and completely neutralized, low molecular, organic acids are: mono-, di- and trisodium citrate, diammonium citrate, monopotassium tartrate, disodium succinate, tetrasodium mellitate $C_{12}(COONa)_4(COOH)_2$.

The maximum level of said water-soluble,

organic acids and/or salts that can be added to the liquid detergent composition of the present invention is not only conditioned by the level of the surface-active detergents present, but primarily by the presence of gelatin, and should not exceed 15% by weight, calculated on the total weight of the composition, and should preferably be below 5% by weight. Some of said organic acid salts can be replaced by inorganic builder salts. The amount of inorganic builder salts, e.g. Naphosphates, Na-carbonates, should preferably not exceed 5% by weight.

Suitable other ingredients or additional compounds which can be added to improve consumer acceptance of the composition of the present invention are: perfumes; dyes; fluorescers; tarnish inhibitors such as benzotriazole or ethylene thiourea; shine improvers such as boric acid or salts thereof in amounts up to 3% by weight; bactericides such as 2-bromo-2-nitro-1,3-propanediol, substituted benziodolium compounds, diphenyl ethers substituted with Cl, Br and/or $-CF_3$, e.g. 3,4-dichloro-4'-trifluoromethyldiphenyl ether; and organic solvents in amounts up to 15% by weight, to improve the pourability of the composition and to enhance the compatibility of different components, as for example C_{2-8} mono- and dialcohols, e.g. butanol, methylpropanol-1 and -2, amylol or pentanol, butanediol as 1,2-, 1,3- and 1,4-butanediol, toluol, benzyl carbinol, ethyleneglycol monobutyl ether, propyleneglycol propyl ether, diethyleneglycol dimethyl ether.

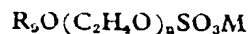
A preferred composition of the invention comprises

(a) from 3% to 15% by weight of a water soluble organic detergent of the general formula



wherein R_n is a straight or branched, saturated or unsaturated aliphatic hydrocarbon radical of from 8 to 24 carbon atoms or an alkylbenzene radical having from 8 to 18 carbon atoms in the alkyl group and M is alkali metal, ammonium or ammonium substituted with 2 or 3 alkyl or hydroxyalkyl groups of 1 or 2 carbon atoms.

(b) from 8% to 25% by weight of a water soluble organic detergent of general formula



where R_n is a straight or branched, saturated or unsaturated aliphatic hydrocarbon radical of from 8 to 18 carbon atoms, n is zero to 12 and M has the meaning set out above

(c) from 2% to 15% by weight of a water soluble, nonionic surface active agent selected from the group consisting of

(1) tertiary amine- or phosphine-oxide of the general formula



where R_1 , R_2 , R_3 and Y have the same meanings as set out above

(2) amides of the general formula



where R_4 is a saturated or unsaturated aliphatic hydrocarbon radical of from 7 to 21 carbon atoms; R_5 is methylene or ethylene and m is 1, 2 or 3.

(3) a condensation product of from 3 to 15 moles of ethylene oxide with one mole of an aliphatic organic compound having from 8 to 24 carbon atoms and a reactive hydrogen atom.

(4) polyethylene glycol condensation products having a molecular weight of from 160 to 1200.

(d) from 0.1 to 5% by weight of a water-soluble gelatin wherein the weight ratio of (b) to (a) is above 0.3:1, the total amount of (a) + (b) + (c) is below 47% by weight and a 0.2% detergent composition concentration in water has a pH which is at most two pH units below and not more than 3 pH units above the iso-electric point of the gelatin used.

The excellent cleaning and, in particular, the superior drainage performance of the liquid detergent composition of the present invention are illustrated in the following tests.

TEST A

Four series A, B, C and D, each of five dish washing liquors defined hereinafter, and three series A', B', C', each of five rinsing liquors are prepared. Each dishwashing liquor of each series contains 0.2% by wt per liter of a dishwashing

composition as defined hereinafter. The rinsing liquors are plain tap water. The water of both the washing and rinsing liquors has a water-hardness of about 3.4 millimoles of $CaCO_3$ per liter. Each washing and rinsing bath contains about 10 liters of water. The temperature of all washing liquors or baths is about 52°C at the beginning and drops to between 42 and 35°C at the end of the washing cycle. The temperature of the rinsing baths fluctuates between 17 and 19.5°C.

In each of said four series of five dishwashing liquors, ten (10) soiled glasses (content: about 25 cl), obtained from a cafeteria, are immersed for two minutes, taken out one by one, rinsed one by one in the rinsing liquor for one minute, and removed for dripping and air-drying (room temperature: about 23°C).

Once the glasses are dry, four experimented graders individually compare the appearance of the glasses, comparing the set of ten glasses washed in the first washing liquor of series A and rinsed in the first rinsing liquor of series A', with the set of ten glasses washed in the first washing liquor of series B and rinsed in the first rinsing liquor of series B'; subsequently, with the set of ten glasses washed in the first washing liquor of series C and rinsed in the first rinsing liquor of series C', etc., the set of ten glasses washed and rinsed in the second washing and rinsing liquor of series A, respectively A', with the set of ten glasses washed and rinsed in the second washing and rinsing liquor of series B, respectively B'; etc. The sets of ten glasses washed in the five washing liquors of series D are not rinsed but air-dried only. The appreciation of the graders as to the difference in overall appearance is expressed in terms of: equal (0), worse (-), better (+), much better (++). Said results are tabulated in Table I.

TABLE I

Series compared	1st washing/rinsing liquor			2nd washing/rinsing liquor		
	AB	AC	AD*	AB	AC	AD*
Grader 1	+	++	0	+	++	-
2	+	++	-	++	+	-
3	++	++	0	++	++	-
4	+	++	-	+	++	0

TABLE I Continued

3rd washing/rinsing liq.			4th washing/rinsing liq.			5th washing/rinsing liq.		
AB	AC	AD*	AB	AC	AD*	AB	AC	AD*
+	++	0	+	++	—	++	+	—
++	++	0	+	+	0	++	++	0
+	++	0	+	++	0	++	++	0
+	++	—	+	++	—	+	++	—

* Series D washed without rinsing.

The liquid dishwashing compositions used in the series A—D are formulated as follows:

Ingredients	Series			
	A	B	C	D
Paraffin sulfonate ammonium salt (average MW of hydrocarbon radical: 196)	10	—	10	10
Coconut alcohol-ethylene oxide (3) sulfate ammonium salt	10	—	10	10
Dimethyldodecylamine	4	4	4	4
Coconut alcohol-ethylene oxide (6) condensate	7	20	7	7
Coconut fatty acid diethanol amide	—	2	—	—
Gelatin (average MW 25 000; iso- electric point about pH 8; Bloom strength about 100)	—	1	1	1
Water				
pH of the washing liquors	7	7	7	7

5 The dishwashing composition of series A is
a representative of an efficient dishwashing
cleaning agent. It is striking, as can be seen
from Table I, that the glasses washed in the
washing liquors of series D (having the same
composition as the washing liquors of series
A, except 1% by wt of gelatin) are not
10 cleaner than those washed and rinsed in the
washing and rinsing liquors of series A, re-
spectively A', although the glasses washed and
rinsed in the washing and rinsing liquors of B
and C, respectively B' and C', are far superior
15 in overall appearance over those washed and
rinsed in washing and rinsing liquors A, re-
spectively A'.

TEST B

20 Four other series E,F,G and H, each of five

dishwashing liquors are prepared, containing
each 0.25% by wt per liter of a dishwashing
composition, whereby the dishwashing liquors
of series E contain the dishwashing
composition of series A, those of series F the
25 dishwashing composition of series B, those of
series G, the one of series C, and those of
series H, the dishwashing compositions of
series D, as described above. Also three series
E',F' and G' of rinsing liquors are prepared. 30
The water used has the same hardness as in
Test A. Each washing and rinsing bath con-
tains about 5 liters of water. The water is 10
cm high in each washing and rinsing bath. The
temperature of the washing liquors is kept 35
at about 42°C. The temperature of the rinsing
baths varies between 30 and 35°C.

A set of four (4) soiled flat dishes (with

glazed surface) obtained from a cafeteria, is washed in each of the five dishwashing liquors of each series E, F, G and H (80 dishes in total) removed from the washing solution and subsequently rinsed in the respective rinsing baths of each series (5 times successively immersed and removed from the bath), except for the five sets of four dishes, each washed in the five dishwashing liquors of series H. The dishes are then removed from the rinsing bath for dripping and air-drying.

The rinsing water on the dishes washed and rinsed in the washing and rinsing liquors of series F and G, respectively F' and G', drains off within 60 seconds, while the water on the dishes washed and rinsed in the washing and rinsing liquors E, respectively E', or washed in the washing liquors of series H, only slowly disappears due to evaporation (10 to 12 minutes are needed to obtain dry dishes).

When washing a set of four soiled dishes as described above, but rinsing them immediately under running tap water ($\pm 16^\circ\text{C}$) instead of immersing them in the rinsing liquors, exactly the same drainage phenomenon is observed for the dishes washed in washing liquors of series F and G, while the dishes washed in the washing liquors of series E and rinsed under running tap water are dry after 10 to 12 minutes only, due to evaporation.

TEST C

Three series K, L, M, each of five dishwashing liquors are prepared containing 0.2% by wt per liter of dishwashing composition formulated as indicated below. The water used in the

washing and rinsing baths has the same hardness as in Test A. The temperature of all washing liquors is kept at 47°C . The temperature of the rinsing baths is between 30 and 36°C . Each bath contains 5 liters of water; the water is 10 cm high in each bath.

In each of the five washing liquors of each series K, L, M, a soiled dish, as described in Test B, is washed, removed from the washing liquor and subsequently rinsed again in the same way as in Test B in the respective rinsing baths.

The liquid dishwashing composition used in series K has the same composition as that used in series A of Test A; the liquid dishwashing composition used in series L has the same composition as that used in series B of Test A; the liquid dishwashing composition of series M is identical to the liquid dishwashing composition used in series B of Test A, except that 1% of a gelatin with an average molecular weight of about 5 000 (having 0 Bloom strength) is used.

The rinsing water on the dishes washed and rinsed in the washing and rinsing liquors of series K, respectively K', M, respectively M', does not drain off but only disappears much later, mainly due to evaporation, while the water on the dishes washed and rinsed in the washing and rinsing liquors of series L, respectively L', drains off within 60 seconds after removal from the rinsing bath.

The following examples serve to illustrate, but not to limit, the novel composition of the present invention. All percentages indicated are by weight.

EXAMPLES	I	II	III	IV	V	VI	VII
(Components in % by wt)	8	4	2	4	2	4	3
Dimethyldodecyl amine oxide							
Coconut alcohol ethylene oxide (6) condensate	15	7	6	7	2	7	6
Diethanol C_{12-16} fatty acid amide	2	—	3	—	2	—	2
Coconut alcohol ethylene oxide (3) sulfate sodium salt	—	10	9	14	10	12	14
C_{13-16} paraffin sulfonate sodium salt	—	10	9	—	9	10	12
C_{12-14} α -olefin sulfonate ammonium salt	—	—	—	12	—	—	—
Triethanolamine	—	—	—	—	—	5	—
Boric acid	—	—	—	—	—	2	1.5
Gelatin *	1	1	1	1	0.75	1	1
Water	----- Balance -----						

* Gelatin: molecular weight 40 000; iso-electric point 8.4, Bloom strength about 100.

EXAMPLE VIII.

A light duty liquid dishwashing detergent composition is prepared, by first mixing the surface active agents in water and adding the gelatin subsequently under stirring, having the following formulation:

5	— C ₁₂ alkyl ethylene oxide (12) sulfate potassium salt	18.6%
	— dodecyl sulfate potassium salt	10%
10	— dodecyl dimethyl amine oxide	5%
	— gelatin (MW about 60 000; iso-electric point about 4.6; Bloom strength about 150)	1.8%
	— potassium toluene sulfonate	8%
15	— water	balance

Such a composition is effective for cleaning dishes, glasses, when utilized in a 0.2% aqueous solution. When so utilized, such a composition imparts shine to said dishes, glasses, after rinsing with water, and minimizes spotting and filming. Such a composition further has commercially acceptable sudsing and mildness characteristics.

Substantially similar dishwashing performance is obtained when the gelatin in the Example VIII composition is replaced with 1.2% by wt of gelatin, having a MW of 80 000, an iso-electric point of about 4.8, and Bloom strength of 220.

EXAMPLE IX.

30	— Coconut ethylene oxide (6) sulfate sodium salt	16%
	— Coconut alcohol sulfate sodium salt	11%
35	— Coconut alkyl dimethyl amine oxide	4.5%
	— Gelatin (MW about 70 000; iso-electric point about 6; Bloom strength about 200)	1%
40	— Potassium toluene sulfonate	8%
	— Water and minors	Balance

Such a composition is physically stable and is effective for cleaning china, glazed tiles, when utilized in a 0.2% aqueous solution. Utilization of such a composition imparts shine to said items and minimizes filming and spotting thereof. Such a composition additionally has commercially acceptable sudsing and mildness characteristics.

Substantially similar dishwashing performance is obtained when the sodium coconut ethylene oxide (6) sulfate of the Example IX composition is replaced with an equivalent amount of potassium coconut ethylene oxide (12) sulfate, ammonium coconut ethylene oxide (12) sulfate, ammonium coconut ethylene oxide (6) sulfate, triethanolamine coconut ethylene oxide (6) sulfate or triethanolamine coconut ethylene oxide (12) sulfate.

Substantially similar dishwashing perfor-

mance is obtained when the coconut alcohol sulfate salt of the Example IX composition is replaced with an equivalent amount of coconut alcohol potassium and ammonium salt.

Substantially similar dishwashing performance is obtained when the coconut alkyl dimethyl amine oxide of the Example IX composition is replaced with an equivalent amount of dimethyldodecyl amine oxide, dimethyltetradecyl amine oxide or cetyldimethyl amine oxide.

Substantially similar dishwashing performance is obtained when in the above-described Example IX composition, the gelatin is replaced with 1.8% by weight of gelatin, having a MW of about 45 000, an iso-electric point of 4.6 and a Bloom strength of about 120, or 0.8% by weight of a gelatine having a MW of about 60 000, an iso-electric point of about 8.2, and a Bloom strength of about 180.

EXAMPLE X.

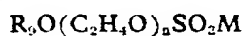
	Dimethyldodecyl amine oxide	4%	
	Coconut alcohol ethylene oxide (6) condensate	5%	85
	Coconut alcohol ethylene oxide (3) sulfate potassium salt	10%	
	C ₁₃₋₁₅ paraffin sulfonate sodium salt	8%	
	Coconut alcohol sulfate potassium salt	4%	90
	Boric acid	1.5%	
	Triethanol amine	5%	
	Ethanol	3%	
	Gelatin (MW 40 000—iso-electric point 8.4; Bloom strength about 100)	1%	95
	Water	Balance	

EXAMPLE XI.

	Dimethyldodecyl amine oxide	4%	100
	Coconut alcohol ethylene oxide (6) condensate	5%	
	Coconut alcohol ethylene oxide (3) sulfate potassium salt	10%	
	C ₁₃₋₁₅ paraffin sulfonate sodium salt	8%	105
	Coconut alcohol sulfate potassium salt	4%	
	Sodium citrate	1%	
	Boric acid	1.5%	110
	Triethanol amine	5%	
	Ethanol	5%	
	Gelatin (MW 40 000—iso-electric point 8.4; Bloom strength about 100)	1%	115
	Water	Balance	

EXAMPLE XII.

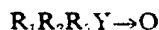
	Dimethyldodecyl amine oxide	4%	
	Polyethylene glycol — molecular weight 400	7%	120
	Coconut alcohol ethylene oxide (3) sulfate ammonium salt	12%	
	C ₁₂₋₁₄ α-olefin sulfonate ammonium salt	10%	



where R_n is a straight or branched, saturated or unsaturated aliphatic hydrocarbon radical of from 8 to 18 carbon atoms, n is zero to 12 and M has the meaning set out above;

- (c) from 2% to 15% by weight of a water soluble, nonionic surface active agent selected from the group consisting of

- (1) tertiary amine- or phosphine-oxide of the general formula



wherein R_1, R_2, R_3 and Y have the same meanings as set out above;

- (2) amides of the general formula



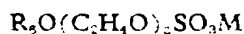
where R_4 is a saturated or unsaturated aliphatic hydrocarbon radical of from 7 to 21 carbon atoms; R_5 is methylene or ethylene and m is 1, 2 or 3, and

- (3) a condensation product of from 3 to 15 moles of ethylene oxide with one mole of an aliphatic organic compound having from 8 to 24 carbon atoms and a reactive hydrogen atom;

- (d) from 2% to 10% of polyethylene glycol condensation products having a molecular weight of from 160 to 1200; and

- (e) from 0.1 to 5% by weight of a water-soluble gelatin wherein the weight ratio of (b) to (a) is above 0.3:1; the total amount of (a)+(b)+(c) being below 47% by weight and a 0.2% detergent composition concentration in water having a pH which is at most two pH units below and not more than 3 pH units above the iso-electric point of the gelatin used.

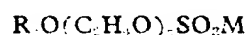
10. A liquid detergent composition according to any one of claims 1—8 containing up to 40% by weight of a water-soluble hydrocarbon sulfate of the general formula



(III)

wherein R_n is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 22 carbon atoms; n is from 0 to 15, and M is a cation; whereby the total amount of nonionic surface-active detergent and hydrocarbon sulfate is at most 48% by weight, calculated on the total weight of the composition.

11. A liquid detergent composition according to claim 10 containing from 2 to 30% by weight of a water-soluble hydrocarbon sulfate of the general formula



(III)

wherein R_n and M have the meaning given above, and n is from 1.5 to 15.

12. A liquid detergent composition as claimed in claim 11 in which n is from 3 to 12.

13. A composition according to claim 10 in which the surface active agent comprises a mixture of from 2—16% by weight of the total composition of tertiary amine oxide and from 1 to 40% by weight of the total composition of water soluble hydrocarbon sulphate which hydrocarbon sulphate contains from 2 to 15% by weight of the total composition of hydrocarbon sulphate in which n is zero, and the gelatin has an iso-electric point at 4.6 to 5 and a Bloom strength of from 50 to 300.

14. A composition according to claim 13 in which that part of the hydrocarbon sulphate in which n is not zero has $n=3$ to 12.

15. A liquid detergent composition according to claim 10 containing from 2% to 15% by weight of a water-soluble hydrocarbon sulfate of the general formula



(III)

wherein R_n and M have the meaning given above, and $n=0$.

16. A liquid detergent composition as claimed in any one of claims 10—15 in which the R_n radical has from 12 to 16 carbon atoms.

17. A liquid detergent composition according to any one of claims 1—8 containing up to 30% by weight of a water-soluble, organic, sulfuric acid reaction product of the general formula



(IV)

wherein R_n is chosen from the group consisting of a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24 carbon atoms; and an alkylbenzene radical having from 8 to 18 carbon atoms in the alkyl group; and M is a cation whereby the total amount of nonionic surface-active detergent and organic sulfuric acid reaction product is at most 48% by weight, calculated on the total weight of the composition.

18. A liquid detergent composition according to claim 17, containing up to 20% by weight of an organic, sulfuric acid reaction product of the general formula R_nSO_3M , wherein R_n and M have the meaning indicated above and whereby the weight ratio of said organic sulfuric acid reaction product (IV) to nonionic surface-active detergent is below 5/1, preferably below 3/1.

19. A liquid detergent composition according to claim 17 or claim 18 in which the R_n aliphatic hydrocarbon radical has from 12 to 18 carbon atoms.

20. A liquid detergent composition according to any one of claims 17—19 in which the R, alkyl benzene radical has from 12 to 16 carbon atoms in the alkyl group.

5 21. A liquid detergent composition as claimed in any one of claims 17—20 in which the organic sulfuric acid reaction product (IV) is present in an amount of 3% to 15% by weight.

10 22. A liquid detergent composition according to any one of claims 17—21 in which the organic, sulfuric acid reaction product (IV) is a C₁₂₋₁₈ n-paraffin sulfonate.

15 23. A liquid detergent composition according to any one of claims 1—8 containing up to 40% by weight of a mixture of a water-soluble hydrocarbon sulfate of the general formula



(III)

20 and a water-soluble organic, sulfuric acid reaction product of the general formula R₇SO₃M (IV) wherein R₆, R₇, M and n have the meaning indicated above; whereby the total amount of nonionic surface-active detergent, hydrocarbon sulfate and organic, sulfuric acid reaction product is at most 48% by weight; and whereby the weight ratio of organic, sulfuric acid reaction product to the sum of the nonionic surface-active detergent and hydrocarbon sulfate is at most 3/1.

30 24. A liquid detergent composition according to claim 23 in which the weight ratio of organic sulfuric acid reaction product to the sum of nonionic surface-active detergent and hydrocarbon sulfate is below 1.5/1.

35 25. A liquid detergent composition according to any one of claims 1—8 and 10—23 containing from 0.5 to 2% by weight of gelatin having an iso-electric point between pH 7 and 8.5, an average molecular weight between 35 000 and 50 000, and gel strength of 80 to 200 Bloom grams; from 4 to 16% of a hydro-soluble nonionic surface active detergent; from

2 to 30% of a water-soluble hydrocarbon sulfate of the general formula



wherein R₆ and M have the meaning given above, and n is from 6 to 12; from 3 to 15% by weight of an organic sulfuric acid reaction product of the general formula R₇SO₃M (IV) wherein R₇ and M have the meaning given above; whereby the weight ratio of said sulfuric acid reaction product to the nonionic surface active detergent is below 2.5/1, while the weight ratio of said sulfuric acid reaction product to the sum of nonionic surface-active detergent and hydrocarbon sulfate is below 1/1.

26. A liquid detergent composition according to any one of claims 1—25 containing up to 15% by weight, calculated on the total weight of the composition of a water-soluble carboxylic acid, or the water-soluble alkali-metal, ammonium-, or substituted ammonium salts thereof.

27. A liquid detergent composition according to claim 26 containing from 2% to 10% by weight, of an alkali-metal salt of an organic acid chosen from the group consisting of citric acid, tartaric acid, succinic acid, benzene hexacarboxylic acid, and ethylene diamine tetra-acetic acid.

28. A liquid detergent composition according to claim 27 containing from 2% to 4% of the alkali metal salt or the organic acid.

29. A liquid detergent composition as claimed in any one of claims 9—28 in which the cation M is sodium or potassium.

30. An aqueous liquid detergent composition substantially as hereinbefore described with reference to any one of the Examples.

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